Determination of volatile organic compounds in ambient air Comparison of methods

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Abstract

Two analytical methods for the determination of benzene vapour in ambient air are compared in this paper. The methods differ from each other in the sampling technique, type of sorbent, method of extraction and method of detection. The investigation of the methods using various techniques for sample analysing showed a significant influence of the way in which the analysis is carried out, on the final result of the analysis. Calculation of the standard deviations, relative standard deviations and confidence intervals allowed for assessment of the precision and repeatability of the methods. Of the two examined methods, that using an automated system of contaminant sampling and thermodesorption was more precise. This method has been applied to measurements of concentrations of benzene, toluene and xylenes in ambient air.
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1. Introduction

Manufacturing processes such as coal coking, various petrochemistry processes, liquid and solid fuels combustion, etc. introduce hazardous volatile organic compounds (VOCs), among them benzene and its homologues, into the atmosphere [1–3]. Benzene belongs to the group constituted by compounds especially harmful to man—it is a carcinogen [4]. In the urban environment benzene and its homologues contribute to formation of the photochemical ozone [5].

Methods for determinations of benzene in ambient air are widely discussed at present. According to the European Union (EU) Directive No. 2000/69/EC the EU members and the candidate countries are obliged to perform continuous monitoring of concentrations of benzene in ambient air. Moreover, the directive imposes the standard on the concentrations of benzene in ambient air defining maximum permissible annual mean concentration of this compound at the level of 5 μg/m^3. Presently, as part of the CEN (Comite Europeen de Normalisation) works, investigation tending towards development of some reference method for determinations of this compound in ambient air is being carried out. Until some uniform method is assumed for all EU countries the application of local, national, procedures in each particular country is allowed.

Methods for determination of concentrations of benzene and its homologues in ambient air comprise stages of analyte enrichment using adsorption methods, desorption of the compounds, and subsequent

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quantitative determinations with the use of the gas chromatography. Activated coal, Carbotrap B, Tenax, Carbopak B and Carbopak B HT, Carbosita B, Ambersorb XE-340 [6–16], are the sorbents most frequently used in analyte enrichment. The choice of the sorbent for collecting samples of benzene and its homologues in ambient air is affected by, among other factors, the desorption method.

The oldest, and also the most frequently used, method of desorption of benzene is the solvent extraction consisting in the liquid–solid extraction [6–8,12,13]. Carbon disulphate (CS_2), purified from benzene, is used as a solvent. As a sorbent in the solvent desorption activated coal is used. Another kind of desorption of benzene vapour is the thermodesorption—in this case Tenax and Carbopaks [9,10,14–16] are most frequently used for analyte enrichment. The quantitative analysis is performed with the use of the gas chromatography using a flame-ionization detection system (GC–FID) or mass spectrometry (GC–MS). Application of a proper configuration sorbent–extraction method directly affects conditions of sampling. Lower sensitivity and higher limits of detection at levels of $\mu g/m^3$ are characteristic of methodologies based on both the analyte enrichment on activated coal and the solvent extraction, and this makes it necessary to collect samples of greater volume, e.g. samples of the volume reaching 60 l. On the other hand, for thermodesorption the detection limit is 0.2 $\mu g/m^3$ and the demanded volume of a sample oscillates around 5.0 l. At present, the passive methods are more and more frequent in measurements of pollutant concentrations in ambient air [17–19].

In the present paper, the results of a comparative investigation of two methods of determination of benzene and its derivatives in air are presented. The first, ''classic'' method (method A), comprised the adsorption on activated coal and the solvent desorption with CS_2 as a solvent. The second one (method B) used an automatic GC with an automated system of sampling, thermodesorber, and analysing system. In both cases the quantitative analyses were performed by means of GC. Also, the applicability of an automatic chromatograph to observing benzene and its derivatives as pollutants of ambient air was evaluated.

2. Materials and methods

2.1. Materials

Carbon disulphate (Sigma–Aldrich, Steinheim, Germany), of spectral purity (GC–FID analysed, no peaks greater than 100 ppb benzene—as assured by the producer).

Before each analytical series CS_2 was analysed by means of GC. If the chromatogram comprised peaks corresponding to compounds with retention times close to retention times of the compounds under investigation, the solvent was not used. To avoid any accidental contamination of the solvent all its dosage operations were performed in a container filled with nitrogen.

Activated carbon, granulation 0.3–0.6 mm was obtained from Merck (Darmstadt, Germany). Prior to sampling the activated carbon had been thermally purified for 6 h in vacuum at the temperature of 200 °C.

The gaseous standard mixture consisted of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene in nitrogen. The mixture was purchased from Linde (Gierchaftsbereich Linde Gas, Hoellriegelskreuth, Linde, Germany); the detailed composition of the mixture is shown in Table 1.

2.2. Analytical background of sorbents

The analytical background was determined for each portion of the purified activated coal. A 150-mg amount of the sorbent was placed in a closed dish where 1 ml of CS_2 was added to it. The contents of the dish were mixed thoroughly for 5 min. After 30 min the extract was analysed using chromatography. If any compounds with retention times close to the retention times of compounds being determined were found in the extract, the purification process of the coal was repeated.

For Carbotrap B the analytical background was determined as follows. A 10-l Tedlar bag was filled with synthetic air, connected to the sampling system, and analysis of air samples was performed. If in the chromatograms peaks proper for compounds with retention times close to the retention times of the

Table 1
Composition of the standard mixture

No.	Compound	Concentration ($\mu g/m^3$)	Retention time (min:s)	
			DB-1	MTX-5
1	Benzene	116	7:46	1:47
2	Toluene	145	10:09	2:56
3	Ethylbenzene	154	12:18	4:17
4	*m*-Xylene	154	13:01	4:24
5	*p*-Xylene	154	13:01	4:24
6	*o*-Xylene	159	13:03	4:50
7	1,2,4-Trimethylbenzene	175	19:49	6:50
8	1,3,5-Trimethylbenzene	175	19:13	6:42

determined compounds were found, bed purification was performed. The purification of the bed consisted of increasing the desorption temperature by 50 °C and maintaining it for the sorbent bed for 5 h. All this time carrier gas was being let through the sampling system.

2.3. Method A

2.3.1. Sampling

A sample for the analysis was prepared by drawing 40 l of the standard mixture through a sorption tube measuring 9 cm×4 mm I.D., packed with 150 mg of purified activated coal, at a flow-rate of 80 1/min.

2.3.2. Preparation of material for analyses

The procedure of preparation of the samples for an analysis was the same as the methodology for determination of the analytical background for purified activated coal. After sampling the sorbent was placed in a vial with a membrane seal of PTFE. Next, 1 ml of pure, with no detectable benzene, carbon disulphate was introduced into the vial, and the whole contents were shaken for 5 min. The solution was analysed after 30 min.

2.3.3. Chromatographic conditions

The analyses, both qualitative and quantitative, were performed on a Star 3400 CX Varian gas chromatograph (Varian Walnut Creek, CA, USA) equipped with a Saturn-3 mass spectrometer and DB-1 capillary column (60 m×0.32 mm I.D., film

thickness 1 μm, produced by J&W Scientific, Folson, CA, USA). The temperature of the column was programmed to increase from 60 to 200 °C at 4 °C/min. The temperature of the injector was 250 °C. The temperature of the source was maintained at 250 °C. The electron impact ionisation conditions were: ion energy −70 eV, emission current −20 μA, scan range from 45 to 600 u, scan rate 1 s/scan, mass defect 60 mu/10 μz, background mass–45 u.

The qualitative analysis was performed by comparing the retention times and the mass spectra registered for the compounds corresponding to the particular peaks in the chromatogram with the mass spectra from catalogues. The quantitative analysis was performed by using selected ion monitoring method (SIM), choosing one or two typical ions for each compound.

The chromatogram of the standard mixture is presented in Fig. 1. The calibration curves for the studied compounds are presented in Fig. 2.

2.4. Method B

2.4.1. Sampling

In method B an automatic chromatograph, comprising a sampling system with a sorption unit, thermodesorber, analytical column, and a Chromato-Sud, model ArmioBTX, flame ionization detector (FID, from Chromato-Sud, Saint-Antoine, France), was applied. A 750-ml sample of gas was automatically taken at the rate of 50 ml/min. Volatile compounds were adsorbed on a Carbotrap B bed (Merck). The sampling system comprised three
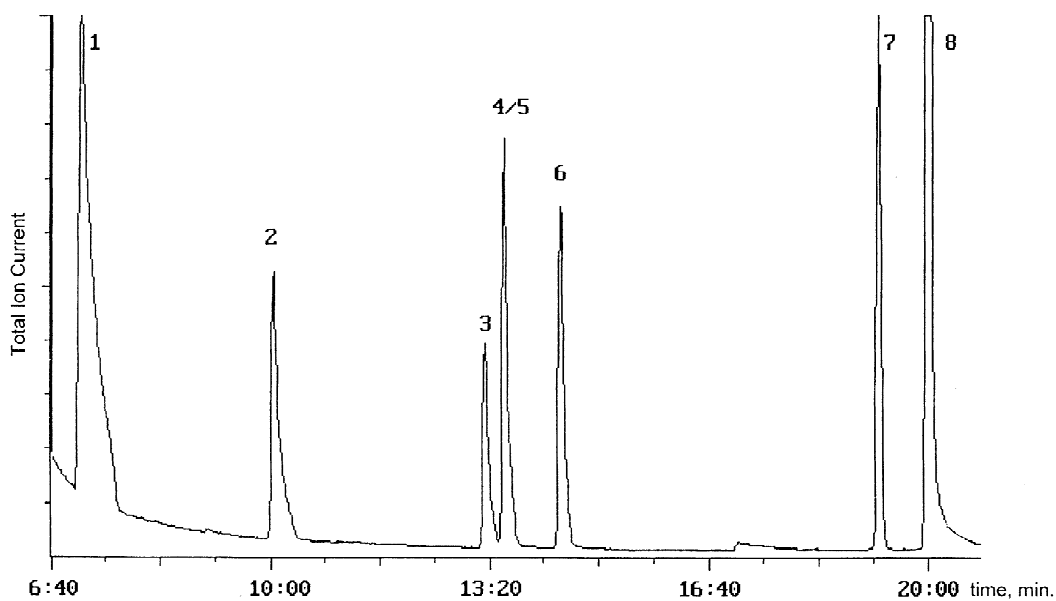
Fig. 1. GC–MS chromatogram of the standard mixture: 1=benzene, 2=toluene, 3=ethylbenzene, 4/5=*m*-, *p*-xylene, 6=*o*-xylene, 7=1,3,5-trimethylbenzene, 8=1,2,4-trimethylbenzene.
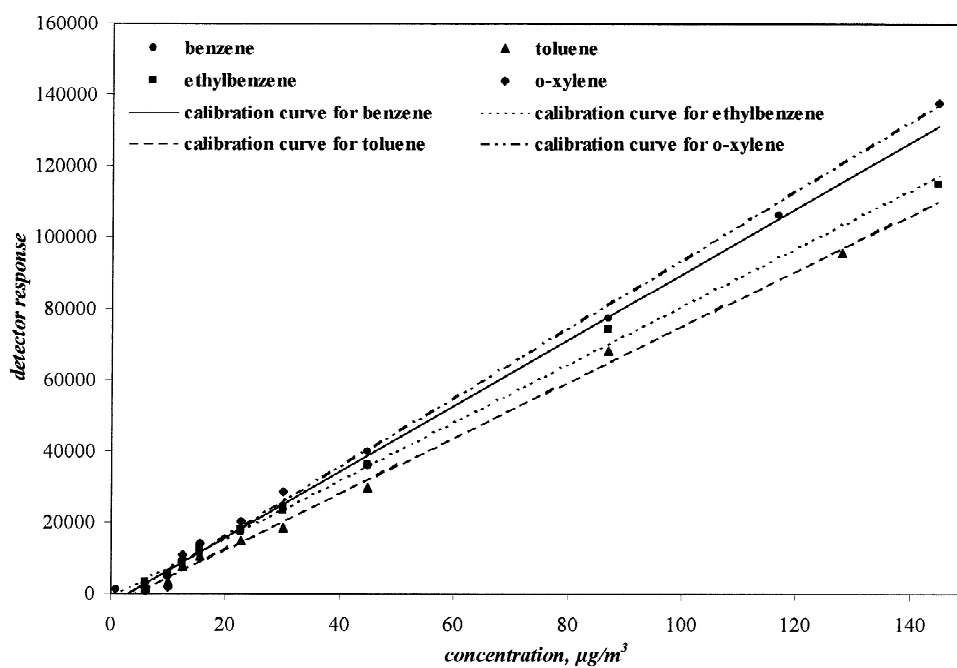

Fig. 2. Calibration curves for benzene, toluene, ethylbenzene and *o*-xylene for method A.

sorption tubes; two tubes worked alternately. While the desorption from one of them occurred, the second one was taking a sample—i.e. sorbing pollutants. The system automatically changed the tubes in steps defined by the timer of the analysis. The single sample drawing was automatically controlled and the volume of sucked-in air was measured for each sample separately. The operating conditions of the chromatograph allow neither particulates nor water in the gas samples.

2.4.2. Thermodesorption

The thermal desorption of analyte lasted 3 min at the temperature of 300 °C. The analyte was dosed to an analytical column through a dosing valve heated up to the temperature of 350 °C. The time of a sample application to the column was 120 s.

2.4.3. Quantitative analysis

The quantitative determination was performed with FID being an integral part of the system. The temperature of the MTX-5 analytical column (9 m×0.52 mm I.D., film thickness 1 μm, (Chromato-Sud) changed from 45 to 150 °C at 20 °C/min and the terminal temperature of the column was maintained for 2 min. The flow-rate of the carrier gas (hydrogen) in the column was 0.5 ml/min. All the time the temperature of the detector was 150 °C.

The determined compounds were identified by their retention times. Quantitative determinations were performed using the external standard method with the standard mixture shown in Table 1.

The chromatogram of the standard mixture is presented in Fig. 3.

2.5. Statistical evaluation of the methods

To evaluate the two methods A and B statistically, each of them was applied ten times to analysis of the standard mixture. The results allowed for the determination of the standard deviations (SDs), relative standard deviations (RSDs) and confidence intervals for the methods. Moreover, the detection limits and detection ranges were determined for both methods. To determine the detection limit the standard mixture was diluted in nitrogen so that each of components of the mixture was at a concentration of 500 ng/m^3. Tables 2 and 3 present the results of these calculations.

3. Results

The results of the investigations showed a influence in the choice of methods for collecting gaseous samples and for extraction to the final result of the determination. Both the SD and RSD values
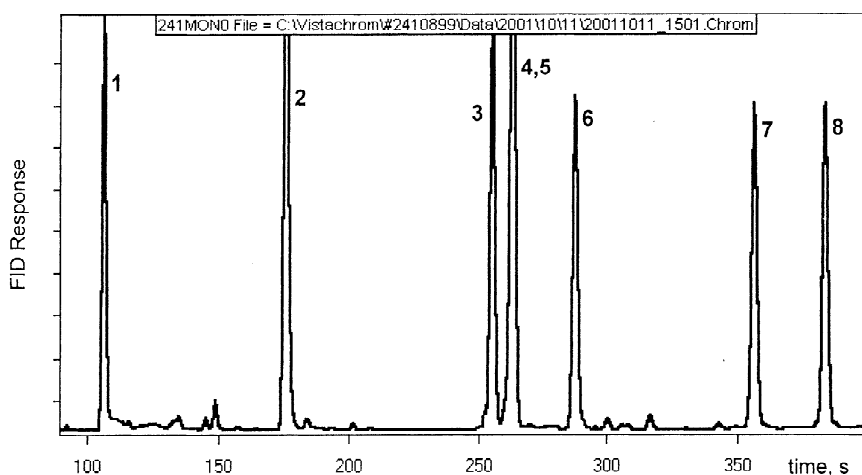

Fig. 3. TD–GC–FID chromatogram of the standard mixture: 1=benzene, 2=toluene, 3=ethylbenzene, 4/5=m-, p-xylene, 6=o-xylene, 7=1,3,5-trimethylbenzene, 8=1,2,4-trimethylbenzene.

Table 2
Precision of the methods A and B for determination of VOCs in air

Compound	Standard deviation ($\mu g/m^3$)		Detection limit ($\mu g/m^3$)	
	Method A	Method B	Method A	Method B
Sampling volume (l)	40	0.750		
Benzene	10.36	0.81	1	0.3
Toluene	12.57	1.00	6	0.4
Ethylbenzene	14.80	1.26	6	0.4
m-+p-Xylene	14.51	1.28	6	0.4
o-Xylene	16.08	1.04	6	0.4
1,2,4-Trimethylbenzene	17.00	1.33	10	0.5
1,3,5-Trimethylbenzene	17.01	1.29	10	0.5

were considerably higher for method A than for the method B. SDs computed for A assumed values from 10 to 17 $\mu g/m^3$ depending on the compound. The confidence intervals defined on the basis of the standard mixture analysis were quite big for method A—12.84 $\mu g/m^3$ for benzene to 21.08 $\mu g/m^3$ for 1,2,5-trimethylbenzene, while for B the greatest value was 1.64 $\mu g/m^3$ (for 1,2,3-trimethylbenzene). In general, the highest random errors occur while sampling, so the high level of RSD of the method A is probably due to the sampling method used. The detection limit of A, using a MS, was 1 $\mu g/m^3$ for benzene, as much as 6 $\mu g/m^3$ for toluene, ethylbenzene and xylenes and 10 $\mu g/m^3$ for trimethylbenzenes. The detection limit of method A for benzene increases up to 5 $\mu g/m^3$ when a flame ionization detection system is used.

Because of favourable precision and detection limit, method B was applied to continuous measurement of benzene, toluene and xylenes (BTX) concentrations in ambient air at a chosen point of the Silesian agglomeration.

The investigation showed considerable diurnal variations of BTX concentrations. Concentration of benzene in air, depending on time of a day, assumed values from 4 to 31.5 $\mu g/m^3$. At the same time concentrations of toluene and m+p-xylenes varied from 4 to 25 $\mu g/m^3$ and from 3 to 17 $\mu g/m^3$, respectively. The smallest differences in measured concentrations between one measurement series were observed for *o*-xylene. Its concentrations in ambient air were from 1 to 3 $\mu g/m^3$. The results are presented in Fig. 4.

4. Discussion

An important criterion for assessing usability of a method for investigations is its detection limit. The preparation of a method for determination of VOCs in air presents many difficulties because of their high volatilities and low concentrations in air. As well, the results of determinations are affected by the properties of the sorbent used, mainly its sorption capacity, depending on the properties of a compound under determination. Investigations carried out in many

Table 3
Relative standard deviations and confidence intervals for the significance level 0.95

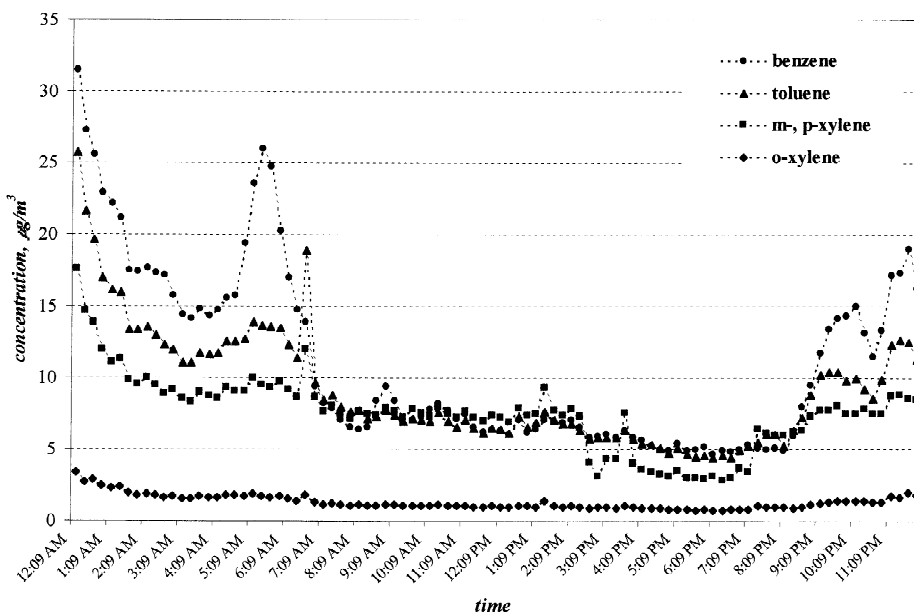| Compound	RSD, $n=10$ (%)		Confidence interval ($\mu g/m^3$)	
	Method A	Method B	Method A	Method B
Benzene	8.93	0.70	116±6.42	116±0.50
Toluene	8.67	0.69	145±7.79	145±0.62
Ethylbenzene	9.61	0.82	154±9.17	154±0.78
m-+p-Xylene	9.42	0.83	308±8.99	308±0.79
o-Xylene	10.44	0.67	159±9.96	159±0.64
1,2,4-Trimethylbenzene	9.71	0.76	175±10.53	175±0.82
1,3,5-Trimethylbenzene	9.72	0.73	175±10.54	175±0.80

Fig. 4. Variability of concentration of BTX on 23rd of December, 2001.

laboratories tend to elaborate more and more precise methods for determination of VOCs in air.

Methods A and B differ from each other in their extraction and detection techniques. Both methods are being applied at present to the monitoring of benzene and its derivatives in air. Application of these methods to the determination of contaminants in ambient air gave considerable differences in their detection limits and precision. The detection limits for the method A are insufficient when measuring pollution of ambient air with VOCs, and especially their continuous monitoring in atmospheric air. Values of SD for investigated compounds were from 12 to 16 times higher, depending on a particular hydrocarbon, for the method A than for B. Moreover, the confidence intervals of the method A for particular compounds are much wider than those of the method B (Table 3). The final results obtained with method A are also significantly affected by a systematic error produced probably by the operator of a sampling system. Another source of errors in method A is the use of CS_2 for extraction. This solvent, providing very good recovery of volatile hydrocarbons from activated coal (about 100% for determined compounds), is very easily contaminated due to its ability to absorb benzene vapour from air. So, when used, it

demands permanent analytical control and must be stored in an atmosphere of inert gas deprived of hydrocarbons. In method A, application of a mass spectrometer based on the selected ion monitoring technique allows for very precise quantitative determinations. The columns used in the investigations, in circumstances of the analysis, did not allow for good separation of *m*- and *p*-xylene.

The detection limit for method B is 0.3 μg/m^3 for benzene, 0.4 μg/m^3 for toluene, ethylbenzene, and xylenes, 0.5 μg/m^3 for trimethylbenzenes. Application of automatic sampling system, thermodesorber and direct introduction of the sample into the analytical column avoids losses due to solvent evaporation as well as eventual random errors arising during manual sampling and preparation of samples for analyses. Moreover, method B, using an automatic chromatograph, is more precise and its results show higher repeatability. For some compounds, RSD values for method B are 10 times lower than those for A. The detection limits of B allow for its application to measurements of volatile pollutants. The use of the method B eliminates harmful CS_2 from laboratory practice and B is much less work-consuming than A, which is of great importance in continuous measurement.

After the EU Directives the permissible mean annual concentration of benzene in ambient air, as maximal safe to humans, is assumed to be 5 $\mu g/m^3$ [20]. Consequently, method A does not comply with the EU Directives, especially as far as its detection limit is concerned, and cannot be applied to environmental problems concerning the quality of the atmospheric air.

Because of diurnal variability of concentrations of the investigated compounds in ambient air some part of concentrations of these compounds would not be detectable by method A. This means that A is not a proper method for observing the dynamics of changes of ambient air quality during the defined period of time. This is why the automatic method B was applied to the assessment of air quality. The results received during a 1-day session of measurements illustrate example dynamics of variability of BTX concentration in ambient air (Fig. 4). The total time of a single analysis, comprising the times of sampling and of the sample analysis, is 20 min; during a 24-h measurement period 96 results of determinations are received.

The possibility of obtaining a large number of results of measurements is essential from the monitoring of pollutants point of view. A complete picture of time variations of concentrations of benzene and its homologues in ambient air, including periods of their oscillating about maximum and minimum values, in some concrete area are possible with method B applied in continuous measurement. Investigations with the use of te method B allow for detection of short-term changes in concentrations of BTX caused by variability of emission from point sources of pollutants.

5. Conclusions

Statistical evaluation of the compared methods showed that the method using an automatic sampling system (method B) has better repeatability and lower detection limits than the classic method A. More-over, B does not demand application of a harmful solvent—CS_2. Application of this method in measuring pollution of ambient air with BTX allows for observing changes in quality of ambient air as dependent on their sources and enables assessment of dynamics of their variations. Method B is easy to use in the laboratory to investigate air quality as well as in field measurements to assess ambient air quality.

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